

AD-A196 217

4

## Sulfide Corrosion of Silver Contacts During Satellite Storage

R. BAUER  
Chemistry and Physics Laboratory  
Laboratory Operations  
The Aerospace Corporation  
El Segundo, CA 90245

23 March 1988

Proposed for  
SPACE DIVISION  
AIR FORCE SYSTEMS COMMAND  
Los Angeles Air Force Base  
P.O. Box 92960, Worldwide Postal Center  
Los Angeles, CA 90045-2960

DTIC  
ELECTED  
JUN 20 1988  
S E D

APPROVED FOR PUBLIC RELEASE;  
DISTRIBUTION UNLIMITED

88 6 17 056

This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-85-C-0086-P00016 with the Space Division, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009-2960. It was reviewed and approved for The Aerospace Corporation by S. Feuerstein, Director, Chemistry and Physics Laboratory. Lt Buford W. Shipley/CWDE was the project officer.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Buford Shipley Jr.

BUFORD W. SHIPLEY, Lt, USAF  
SD/CWDE

Raymond M. Leong

RAYMOND M. LEONG, Major, USAF  
Deputy Director, AFSTC West Coast Office  
AFSTC/WCO OL-AB

## UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

## REPORT DOCUMENTATION PAGE

|   |  |   |                            |
|---|--|---|----------------------------|
| 1a. REPORT SECURITY CLASSIFICATION<br>Unclassified  |  | 1b. RESTRICTIVE MARKINGS  |                            |
| 2a. SECURITY CLASSIFICATION AUTHORITY   |  | 3. DISTRIBUTION/AVAILABILITY OF REPORT<br>Approved for public release;<br>distribution unlimited.   |                            |
| 2b. DECLASSIFICATION / DOWNGRADING SCHEDULE   |  |   |                            |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S)<br>TR-0086A(2945-03)-7  |  | 5. MONITORING ORGANIZATION REPORT NUMBER(S)<br>SD-TR-88-53  |                            |
| 6a. NAME OF PERFORMING ORGANIZATION<br>The Aerospace Corporation<br>Laboratory Operations   | 6b OFFICE SYMBOL<br>(if applicable)      | 7a. NAME OF MONITORING ORGANIZATION<br>Space Division   |                            |
| 6c. ADDRESS (City, State, and ZIP Code)<br>El Segundo, CA 90245   |  | 7b. ADDRESS (City, State, and ZIP Code)<br>Los Angeles Air Force Base<br>Los Angeles, CA 90009-2960   |                            |
| 8a. NAME OF FUNDING/SPONSORING<br>ORGANIZATION  | 8b OFFICE SYMBOL<br>(if applicable)      | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER<br>F04701-85-C-0086-P00016  |                            |
| 8c. ADDRESS (City, State, and ZIP Code)   |  | 10. SOURCE OF FUNDING NUMBERS   |                            |
|   |  | PROGRAM<br>ELEMENT NO.  | PROJECT<br>NO.             |
|   |  | TASK<br>NO.   | WORK UNIT<br>ACCESSION NO. |
| 11. TITLE (Include Security Classification)<br>Sulfide Corrosion of Silver Contacts During Satellite Storage  |  |   |                            |
| 12. PERSONAL AUTHOR(S)<br>Bauer, Reinhold   |  |   |                            |
| 13a. TYPE OF REPORT   | 13b. TIME COVERED<br>FROM _____ TO _____ | 14. DATE OF REPORT (Year, Month, Day)<br>1988 March 25  | 15. PAGE COUNT<br>12       |
| 16. SUPPLEMENTARY NOTATION  |  |   |                            |
| 17. COSATI CODES  |  | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)<br>Silver Storage<br>Silver sulfide Electrical noise<br>Corrosion |                            |
| 19. ABSTRACT (Continue on reverse if necessary and identify by block number)<br>Delays in satellite launchings may require satellites to be stored on the ground for up to 6 years, and, in some instances, electrical "scratchy" noise on pure silver electrical connectors may develop in as little as 6 months. This problem has been attributed to the growth of silver sulfide, Ag <sub>2</sub> S, a semiconductor, on the silver contact surfaces. We offer suggestions that could improve storage specifications for satellites where Ag <sub>2</sub> S might be reduced to a level (thickness) where it does not pose a problem. This review of Ag <sub>2</sub> S growth might also be applicable to other satellite components where Ag is present, e.g., mirrors.<br>Key words: Corrosion Film<br>Electric Contacts (1. u.) |  |   |                            |
| 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT<br><input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS  |  | 21. ABSTRACT SECURITY CLASSIFICATION<br>Unclassified  |                            |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL   |  | 22b. TELEPHONE (Include Area Code)  | 22c. OFFICE SYMBOL         |

## I. INTRODUCTION

Increasing delays are expected in satellite launchings, requiring satellites to be stored on the ground for possibly up to 6 years. In some instances, electrical "scratchy" noise on pure silver electrical connectors develops in as little as 6 months. This problem has been attributed to the growth of silver sulfide,  $\text{Ag}_2\text{S}$ , a semiconductor, on the silver contact surfaces. In reviewing the literature, we have set forth suggestions that could improve storage specifications for satellites where  $\text{Ag}_2\text{S}$ , although not entirely eliminated, might be reduced to a level (thickness) where it does not pose a problem. This review of  $\text{Ag}_2\text{S}$  growth might also be applicable to other satellite components where Ag is present, e.g., mirrors.

## II. DISCUSSION

### A. CORROSIVE FILM GROWTH ON SILVER

The sulfidation of silver depends primarily on two parameters: the amount of reduced sulfur gases present and the water vapor (humidity) at the silver surface.

Silver sulfide is the most common corrosive film formed indoors on silver; outdoors, corrosion films usually contain a mixture of silver chloride, silver sulfate, and silver sulfide.<sup>1</sup> Silver does not react with oxygen to form silver oxide at ambient conditions.<sup>2</sup> The major sulfur-containing compounds in the environment are listed in Table 1,<sup>3</sup> with  $\text{H}_2\text{S}$  and carbonyl sulfide (OCS) responsible for the most silver sulfidation.  $\text{H}_2\text{S}$ , sulfur dioxide ( $\text{SO}_2$ ), and to a lesser extent carbon disulfide ( $\text{CS}_2$ ), dominate the urban areas, but  $\text{SO}_2$  and  $\text{CS}_2$  sulfidation of silver is relatively slow or nonexistent.<sup>4-7</sup> OCS is the most abundant sulfur-containing compound in nonurban areas, having a nearly uniform concentration throughout the globe. Studies of the effects of various gases on the sulfidation of silver, performed in the laboratory, cannot exactly emulate the type of sulfidation found in the field. A multitude of chemical compounds can be formed in field environments, each with its specific hardness and conductivity. However, since satellites are stored in controlled indoor environments rather than in the field, papers that deal with laboratory rather than field results should be of greater significance.

TABLE 1. Concentration of Atmospheric Sulfur Gases (ppb)

| Species                          | Urban, Industrial Areas | Remote Areas   |
|----------------------------------|-------------------------|----------------|
| H <sub>2</sub> S                 | 0.02 to 5.00            | 0.005 to 0.050 |
| CS <sub>2</sub>                  | 0.07 to 0.37            | 0.025 to 0.045 |
| CH <sub>3</sub> SCH <sub>3</sub> | No data                 | 0.042 to 0.062 |
| OCS                              | 0.43 to 0.57            | 0.430 to 0.570 |
| SO <sub>2</sub>                  | 1.00 to 1000            | 0.050 to 0.120 |

The importance of reducing the amount of sulfur-containing gases in the presence of silver was demonstrated by Bennett et al.<sup>8</sup> A film of 60 Å (angstrom units) was grown in 1 month in normal laboratory air of 42% relative humidity (RH) and 0.2 ppb H<sub>2</sub>S. The fact that the film grew slower at night than during the day was attributed to the more than usual number of people in the laboratory and the extra forepumps operating which contained a small amount of H<sub>2</sub>S in their pumping oil.<sup>9</sup> The film growth rate was cut in half by storage in an electron microscope room, and storage in a plastic bag with positive nitrogen pressure stopped film growth completely. Samples stored in the latter condition for 2 months showed less than 5 Å film growth, which was attributed to occasional removal of samples from the plastic bag for thickness measurements. It also appears that storing samples in a vacuum of <70 Torr slowed film formation. Bennett's evaporated silver film, (1,1,1) plane, although less reactive than thermally etched or polished silver surfaces, demonstrates that reducing the amount of sulfur-containing gases is of primary importance in reducing the sulfidation rate of silver. In a static gas flow situation, once the original corrosive gas is depleted, the film growth stops.

Increasing the % RH clearly accelerated the tarnish growth rate, as shown in Fig.1, where the thickness is plotted as a function of total exposure defined as parts per million H<sub>2</sub>S times hours exposed. Since each paper used a different analytical technique (scanning electron microscope with energy dispersive x-ray,<sup>10</sup> x-ray fluorescence,<sup>4</sup> radioactive H<sub>2</sub>S<sup>35</sup>,<sup>1</sup> and electrolytic reduction<sup>16</sup>) to measure the sulfide film thickness, some discrepancy in the

|                    |                                     |
|--------------------|-------------------------------------|
| Accession For      |                                     |
| NTIS               | GRA&I                               |
| DTIC TAB           | <input checked="" type="checkbox"/> |
| Unannounced        | <input type="checkbox"/>            |
| Justification      |                                     |
| By _____           |                                     |
| Distribution/      |                                     |
| Availability Codes |                                     |
| Dist               | Avail and/or<br>Special             |

**A-1**

DTIC  
COPY  
INSPECTED  
4

SQUARES < 5 % RH      ROOM TEMP.

CIRCLES > 75% RH      ROOM TEMP.

TRIANGLE 85% RH      125°F (52°C)

NUMBERS ON LINES DENOTE REFERENCES

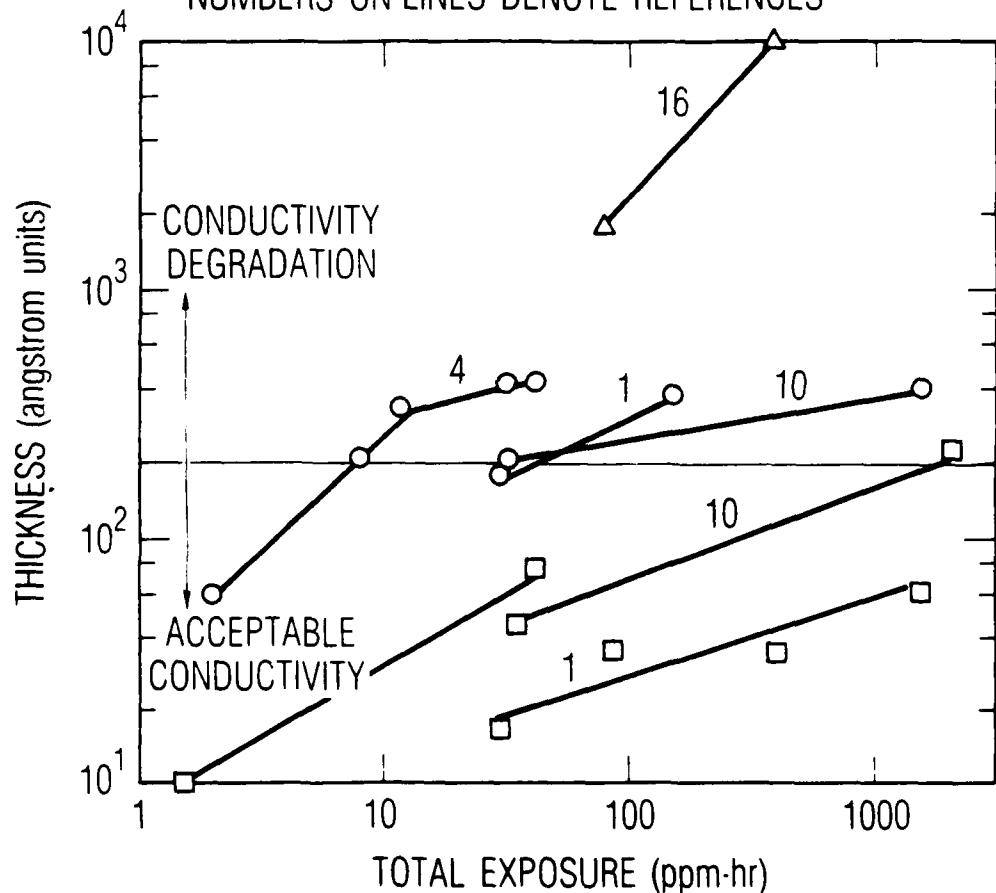


Figure 1. Silver Sulfide Growth as a Function of Total  $\text{H}_2\text{S}$  Exposure and Humidity.

rate of formation is to be expected. Emphasis should therefore be directed toward comparing the high and low humidity results within each paper. A reduction from 75% RH to <5% RH should lower the growth rate by a factor of 3 to 10 times. Pope<sup>4</sup> found that the rate of growth was not significantly different between films grown at 0.5 Torr and 2 ppm water vapor, ~3% RH and ~0.01% RH, respectively; both of these films grew at one-eighth the rate of those at 14 Torr water vapor, ~75% RH, after a total exposure of 30 ppm-hour. Using a complex mixture of gases, Rice<sup>5</sup> found tarnish growth to be independent of RH between 30 and 80% RH, whereas Lorenzen<sup>7</sup> found the growth rate to increase significantly between 30 and 50% RH.

#### B. GROWTH MECHANISM AND ELECTRICAL PROPERTIES

The mechanism for silver sulfidation is not completely understood, but the general belief is that sulfur rather than H<sub>2</sub>S is the corrosive constituent that reacts with silver<sup>7</sup> and that water provides an effective medium for the H<sub>2</sub>S oxidation to sulfur.<sup>7,10,11</sup> When several monolayers of water are on the surface, the H<sub>2</sub>S dissolves easily<sup>12</sup> and dissociates, with sulfur attacking the silver at surface defects such as facets, steps, and edges.<sup>13</sup> In a "dry" surface condition where there is less than one monolayer of water on the surface, the initial step is dissociative adsorption of H<sub>2</sub>S onto the metal lattice at a surface defect. OCS is generally noncorrosive under dry conditions at room temperature, but in the presence of water rapidly decomposes.<sup>3</sup> Stoichiometrically, this can be expressed as OCS + H<sub>2</sub>O → H<sub>2</sub>S + CO<sub>2</sub>, although the reaction probably has a number of intermediate steps. The mechanism of OCS dry sulfidation is thought to be similar to the H<sub>2</sub>S case.

Silver sulfide tends to grow not as a uniform film but rather as clumps.<sup>11</sup> The clumps per unit area do not change with time but become thicker and grow laterally.<sup>8</sup> Extrapolating these data would indicate that not until 150 Å does the surface coverage become 100%. Initially, sulfur rapidly attacks the silver surface. Once the sulfide layer becomes continuous, growth takes place on the sulfide surface. Thereafter, sulfidation is limited by the rate at which the sulfur-containing gas is supplied to the surface<sup>14</sup> or the rate at which silver, a highly mobile ion,<sup>15</sup> diffuses through the sulfide layer.

Silver sulfide has two crystal forms:  $\beta$ -  $\text{Ag}_2\text{S}$  exists below 177°C, and  $\alpha$  -  $\text{Ag}_2\text{S}$  above 177°C. It is an n-type semiconductor with the conductivity increasing with temperature in the  $\beta$  form. Above 177°C, the conductivity increases sharply.

### III. CONCLUSION

Most electrical connectors can tolerate some sulfide on their surfaces. Although the thickness at which tarnish begins to noticeably degrade the electrical properties of the circuit is not well established, 200 Å can be considered a reasonable thickness where conductivity problems can begin for the following reasons:

1. The silver sulfide layer becomes continuous at about 150 Å.
2. Silver sulfide grown on a pure silver surface is soft and malleable, being easily pushed aside even under low load. This would allow enough microasperity contacts to give a low contact resistance.<sup>12</sup>
3. Tests examining the electrical conductivity of silver sulfide,<sup>14,16,17</sup> although widely varying, seem to indicate that 200 Å would be a reasonably conservative estimate of the thickness at which electrical properties begin to deteriorate.

Reducing the amount of sulfur gas is of primary importance in slowing or eliminating the growth of the corrosion film. Failure to reduce or minimize the growth of the corrosion film on satellite components where silver is the major constituent can lead to a system failure, e.g., electrical contacts for power or signal slip-ring units. Methods to reduce the sulfur gas concentrations can range from placing the satellite in a chamber with a positive nitrogen flow; placing it in a soft vacuum <70 Torr; or placing it in a purged, sealed chamber. Decreasing the water vapor, % RH, will also reduce the growth rate of the sulfide films, although it is not clear at what % RH an improvement begins. Indications are that at <30% RH the rate of film formation begins to decrease. If the storage environment has been characterized ( $\text{H}_2\text{S}$  concentration and % RH), then Fig. 1 can be used to calculate the approximate "safe" storage time where the electrical contact performance remains acceptable.

Equally important as the storage time after assembly are the prestorage environmental conditions present during the manufacturing, assembly, and

storage in stock of the electrical connectors. It is stressed that these results are only applicable to sulfidation on pure silver surfaces. Sulfidation of silver alloys will most likely give different results, since the products of the sulfided alloys have different electrical and hardness characteristics.

## REFERENCES

<sup>1</sup>Crossland, W. A. and Knight, E., "The Tarnishing of Silver/Palladium Surfaces and its Effect on Contact Resistance in Low Energy Circuits," Holm Seminar on Electrical Contact Phenomena, Illinois Institute of Technology, 1973, pp. 248-264.

<sup>2</sup>Czanderna, A. W., "Adsorption of Oxygen on Silver," Journal of Physical Chemistry Vol. 68, 1964, pp. 2765-2772.

<sup>3</sup>Greadel, T. E., "Carbonyl Sulfide: Potential Agent of Atmospheric Sulfur Corrosion," Science, Vol. 212, 8 May 1981, pp. 663-665.

<sup>4</sup>Pope, D., Gibbens, H. R., and Moss, R. L., "The Tarnishing of Silver at Naturally Occurring H<sub>2</sub>S and SO<sub>2</sub> Levels," Corrosion Science, Vol. 8, 1968, pp. 883-887.

<sup>5</sup>Rice, D. W., Peterson, P., Rigby, E. B., Phipps, P. B. P., Cappell, R. J., and Tremoureaux, R., "Atmospheric Corrosion of Copper and Silver," Journal of Electrochemical Society, Vol. 128, 1981, pp. 275-284.

<sup>6</sup>Franey, J. P., Kammlot, G. W., Greadel, T. E., "The Corrosion of Silver by Atmospheric Sulfurous Gases," Corrosion Science, Vol. 25, 1985, pp. 133-143.

<sup>7</sup>Lorenzen, J. A., "Atmospheric Corrosion of Silver," Proceedings of the Institution of Environmental Science, Vol. 17, 1971, pp. 110-116.

<sup>8</sup>Bennett, H. E., Peck, R. L., Burge, D. K., and Bennett, J. M., "Formation and Growth of Tarnish on Evaporated Silver Films," Journal of Applied Physics, Vol. 40, 1969, pp. 3351-3360.

<sup>9</sup>Holland, L., "A Review of Some Recent Vacuum Studies," Vacuum, Vol. 20, 1970, pp. 175-192.

<sup>10</sup>Greadel, T. E., Franey, J. P., Gualtieri, G. J., Kammlott, G. W., and Malm, D. L., "On the Mechanism of Silver and Copper Sulfidation by Atmospheric H<sub>2</sub>S and OCS," Corrosion Science, Vol. 25, 1985, pp. 1163-1180.

<sup>11</sup>Reagor, B. T. and Sinclair, J. D., "Tarnishing of Silver by Sulfur Vapor: Film Characteristics and Humidity Effects," Journal of Electrochemical Society, Vol. 128, 1981, pp. 701-705.

<sup>12</sup>Stephen, H. and Stephen, T., Solubilities of Inorganic and Organic Compounds I, Part 1. Macmillan, New York, 1963.

<sup>13</sup>Allpress, J. G. and Sanders, J. V., "The Influence of Surface Structure on a Tarnishing Reaction," Philosophical Magazine, Vol. 10, 1964, pp. 827-836.

<sup>14</sup>Abbott, W. H., "The Effects of Substrate in the Contact Resistance of Tarnish Films," IEEE Transactions on Parts, Hybrids, and Packaging, Vol. PHP-7, 1971, pp. 6-10.

<sup>15</sup>Russ, G. J., "Electrical Characteristics of Contacts Contaminated with Silver Sulfide Film," IEEE Transactions on Parts, Materials, and Packaging, Vol. PMP-6, 1970, pp. 129-137.

<sup>16</sup>Chiarenzelli, R. V., "Tarnish Films on Electric Contact Materials," Proceedings of the Third Symposium of Electrical Contacts, University of Maine, 1966, pp. 86-93.

<sup>17</sup>Crossland, W. A., Knight, E., and Wright, C. R., "The Accelerated Tarnish Testing of Contacts and Connectors Employing Silver Alloy Contacts," Holm Seminar on Electric Contact Phenomena, Illinois Institute of Technology, 1973, pp. 265-282.

## LABORATORY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security projects, specializing in advanced military space systems. Providing research support, the corporation's Laboratory Operations conducts experimental and theoretical investigations that focus on the application of scientific and technical advances to such systems. Vital to the success of these investigations is the technical staff's wide-ranging expertise and its ability to stay current with new developments. This expertise is enhanced by a research program aimed at dealing with the many problems associated with rapidly evolving space systems. Contributing their capabilities to the research effort are these individual laboratories:

Aerophysics Laboratory: Launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion, propellant chemistry, chemical dynamics, environmental chemistry, trace detection; spacecraft structural mechanics, contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; cw and pulsed chemical and excimer laser development including chemical kinetics, spectroscopy, optical resonators, beam control, atmospheric propagation, laser effects and countermeasures.

Chemistry and Physics Laboratory: Atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes, sensor out-of-field-of-view rejection, applied laser spectroscopy, laser chemistry, laser optoelectronics, solar cell physics, battery electrochemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, thermionic emission, photo-sensitive materials and detectors, atomic frequency standards, and environmental chemistry.

Computer Science Laboratory: Program verification, program translation, performance-sensitive system design, distributed architectures for spaceborne computers, fault-tolerant computer systems, artificial intelligence, microelectronics applications, communication protocols, and computer security.

Electronics Research Laboratory: Microelectronics, solid-state device physics, compound semiconductors, radiation hardening; electro-optics, quantum electronics, solid-state lasers, optical propagation and communications; microwave semiconductor devices, microwave/millimeter wave measurements, diagnostics and radiometry, microwave/millimeter wave thermionic devices; atomic time and frequency standards; antennas, rf systems, electromagnetic propagation phenomena, space communication systems.

Materials Sciences Laboratory: Development of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; non-destructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures as well as in space and enemy-induced environments.

Space Sciences Laboratory: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation.